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# Studies on the electrochemical reduction and coupled homogeneous reactions of cinnamaldehyde in acetonitrile

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ABSTRACT

An in-depth investigation on the redox reactions of cinnamaldehyde in acetonitrile was carried out using cyclic, linear sweep, and rotating disk electrode voltammetry in conjunction with controlled potential electrolysis and digital simulations. Overall, it was found that cinnamaldehyde displays a similar reduction behavior to retinal (an aldehyde form of vitamin A), and can be reduced by two consecutive one-electron processes to initially form its radical anion ($E_p^{red} \approx -1.95$ vs. $(Fc/Fc^+)$/V, where $E_p^{red}$ refers to the cathodic peak potential and Fc = ferrocene), and then its dianion ($E_p^{red} \approx -2.50$ vs. $(Fc/Fc^+)$/V). Both reduction processes had limited chemically reversibility even when examined at relatively fast scan rates and low temperatures. Notably, voltammetry and electrolysis experiments revealed that the electrochemical reduction critically depends on the amount of cinnamaldehyde used. At high concentrations, the radical anions have a propensity to undergo a heterodimerization reaction with the starting material to form a radical anionic dimer which could be voltammetrically detected at fast scan rates. Nevertheless, the experimental data also indicated a number of other homogeneous reactions involving the reduced species (radical anion and dianion) which were modeled by digital simulations to determine the electrochemical and kinetic parameters affiliated with all of the heterogeneous electron transfer and homogeneous reaction steps.



## 1. Introduction

Cinnamaldehyde is a biologically active compound (Scheme 1), found in the essential oils of the genus *Cinnamomum*, which is responsible for the distinctive aroma and flavor of cinnamon [1–4].

Although it is most extensively employed as a flavorant, fragrance, and additive in the food and cosmetic industries [1–4], numerous studies have also shown that cinnamaldehyde possesses many qualities that are valuable for unconventional applications. For example, cinnamaldehyde has been demonstrated to exhibit anticorrosion [5–8], antidiabetic [9,10], antimicrobial [11–14], and antitumor [15–18] properties. It is unsurprising, therefore, that the vast utility and usage of this natural product (global consumption is estimated at >100 metric tonnes annually [1]) has also encouraged a myriad of research on its other facets including its detection [19–22], metabolism [23], toxicity [24–26], and others [27–31].

Nevertheless, there are comparatively fewer reports that have focused on cinnamaldehyde's electrochemical behavior. Since many compounds can undergo electron transfer reactions, a comprehensive understanding of cinnamaldehyde's redox chemistry may aid in uncovering more information about its biological features and functions. In particular, electrochemical methods are useful because they can offer information on the number of electrons involved (along with the order of their transfer), which will be essential in deducing complex redox reaction mechanisms [32–35].

The existing electrochemical studies on cinnamaldehyde were mainly conducted in aqueous or protic media using polarography. In these accounts, it was generally recognized that cinnamaldehyde undergoes two stages of reduction. Despite initial suggestions [36–39], it was established that the first reduction involves two-electrons/two-protons ($+2e^-/+2\,H^+$) and engages the alkene bond of the compound to produce a saturated aldehyde (albeit with slight variations to the exact electron/proton transfer sequences at low and high pH), while the second process was ascribed to a further $+2e^-/+2\,H^+$ reduction of the aldehydic group to yield a saturated alcohol [40–43]. In contrast, other works have described that the reduction inextricably involves dimerization reactions which can either furnish a mixture of dimeric products [44,45], couple at the aldehyde functionality to form a pinacol [45], or join in a "head to tail" fashion to generate tetrahydrofuranol products [46], depending on the composition of the test solution.

Based on the above considerations, the present study was initiated to carry out a detailed examination on the electrochemistry of cinnamaldehyde in acetonitrile ($CH_3CN$). The use of an aprotic organic solvent is intended to provide a more lipophilic environment, which more closely mimics what liposoluble biological molecules (e.g. cinnamaldehyde) might experience in the body [32]. In addition, the relatively low water content of aprotic organic media generally allows

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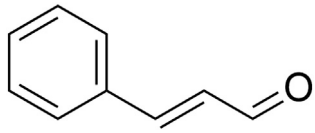

**Scheme 1.** Chemical structure of trans-cinnamaldehyde.

for simpler electrochemical phenomena; such as reducing the likelihood of hydrolysis reactions occurring immediately following reduction, thereby potentially increasing the lifetimes of reactive intermediate(s) [47]. Hence, we report herein the use of a combination of electrochemical and digital simulation techniques to facilitate an in-depth delineation of cinnamaldehyde's reduction reactions.

## 2. Materials & methods

### 2.1. Chemicals & reagents

Unless otherwise specified, all chemicals and reagents were purchased from commercial sources and used as received. Trans-cinnamaldehyde (98 + %) was obtained from Alfa-Aesar. Acetonitrile (HPLC grade) was purchased from Anhui Fulltime Solvents & Reagents Co., Ltd., ethanol (ACS grade) and diethyl ether (ACS grade) from Merck, and *N*,*N*-dimethylformamide (HPLC grade) from VWR. The supporting electrolyte tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$) was prepared by reacting equal molar amounts of a 40% aqueous solution of $Bu_4NOH$ (Alfa-Aesar) with a 65% aqueous solution of $HPF_6$ (Alfa-Aesar), washing the precipitate with hot water, recrystallizing three times from hot ethanol, and then drying in vacuo at 413 K for 6 h.

### 2.2. Voltammetry

Voltammetric experiments were conducted with a computer-controlled Metrohm Autolab PGSTAT302N potentiostat using a three electrode system.

For cyclic voltammetry experiments, working electrodes were 1-mm diameter planar glassy carbon (GC) disks (Cypress Systems), used in conjunction with a platinum wire auxiliary/counter electrode (Metrohm) and a silver wire miniature reference electrode (Cypress Systems) that is connected to the test solution via a salt bridge containing 0.5 M $Bu_4NPF_6$ in $CH_3CN$. Variable temperature cyclic voltammetric experiments were carried out in a Metrohm jacketed glass cell and the temperatures controlled by a Julabo FP89-HL ultralow refrigerated ethanol circulating bath. Rotating disk electrode voltammetry experiments were done using a Metrohm Autolab RDE-2 rotator and a 3-mm diameter planar glassy carbon electrode (Metrohm), in conjunction with the aforementioned instrumentation.

Prior to each voltammetric scan, all solutions used were deoxygenated by purging with high purity argon gas. The working electrodes were cleaned by polishing with alumina oxide (grain size 0.3 μm) slurry on a Buehler Ultra-pad polishing cloth, rinsing with ultrapure water, acetone, and then dried. Accurate potentials were obtained by using ferrocene as an internal standard, which was added to the test solution at the end of the experiments.

### 2.3. Controlled potential electrolysis

Electrolysis experiments were conducted in a two-compartment electrolysis cell separated by a sintered glass frit with a porosity no. 5 (1.0–1.7 μm). Identically sized GC cylinders were used as the working and auxiliary electrodes and symmetrically arranged with respect to each other with a silver wire reference electrode, isolated via a salt bridge containing 0.5 M $Bu_4NPF_6$ in $CH_3CN$, that was positioned to within 2 mm of the surface of the working electrode. The solutions in both electrode compartments were 25 mL each and simultaneously deoxygenated and stirred using bubbles of argon gas. The number of electrons transferred during the bulk electrolysis process was calculated from

$$N = Q/nF \quad (1)$$

where N = number of moles of starting compound, Q = charge (C), n = number of moles of electrons, and F is Faraday's constant (96,485 C $mol^{-1}$).

### 2.4. NMR Analysis of electrolyzed solution

$^1H$ and $^{13}C$ NMR spectra were measured on a Bruker Avance 500 (500 MHz) NMR spectrometer. Chemical shifts (ppm) were recorded using tetramethylsilane (TMS, 0.00 ppm) as the internal reference standard and referenced to $CD_3CN$, the solvent used. $CD_3CN$ was acquired from the Cambridge Isotope Laboratories Inc. The electrolyte ($Bu_4NPF_6$) was removed prior to NMR analysis of the one-electron electrolyzed solutions of cinnamaldehyde by first evaporating $CH_3CN$ under reduced pressure, dissolving the crude electrolyte-products in a mixture of DMF/water (5:3 ratio), extracting with diethyl ether, washing the organic layer with brine, and drying over anhydrous sodium sulfate [48].

### 2.5. Digital simulations

Digital simulation modeling of the CV data was performed using a DigiElch electrochemical simulation software package (DigiElch 7) purchased from Gamry Instruments.

## 3. Results & discussion

### 3.1. Electrochemical reduction of cinnamaldehyde in acetonitrile

We had previously reported that retinal (R), a form of vitamin A with some structural resemblances to cinnamaldehyde (unsaturated aldehyde), can be electrochemically reduced by two sequential one-electron steps into its radical anion ($R^{\bullet-}$) and dianion ($R^{2-}$) in $CH_3CN$ [49,50]. At a glassy carbon (GC) electrode, and using a scan rate of 0.1 V $s^{-1}$, retinal exhibits the presence of two successive reduction/cathodic processes (waves 1 & 2) at ca. −1.82 and −2.15 vs. ($Fc/Fc^+$)/V respectively (Fig. 1a). Although both cathodic reactions display a corresponding oxidative peak in the return sweep of the CV (waves 3 & 4), they are only moderately chemically reversible since the oxidative to reductive peak current ratios ($I_p^{Ox}/I_p^{red}$) for both redox couples are ≪1. Nonetheless, halting the forward potential scan to allow only a single reduction to occur improves the chemical reversibility of the first process, as depicted by the more pronounced size of wave 4.

Preliminary CV scans of cinnamaldehyde under the same conditions disclosed some similarities to the voltammetric behavior of retinal. On the forward scan, cinnamaldehyde likewise presents two successive cathodic processes (waves I & II) at ca. −1.95 and −2.50 vs. ($Fc/Fc^+$)/V respectively (Fig. 1b). Conversely, however, it was found that considerably smaller corresponding anodic currents (waves III & IV) were measured when the scan direction was reversed; especially for wave IV. Moreover, a restriction of the scan's potential range did not appear to benefit the chemical reversibility of the first reduction step.

### 3.2. Cyclic voltammetry at varied scan rates

To further investigate the electrochemical reduction of cinnamaldehyde, CV experiments were next conducted at varied scan rates (Fig. 2). Overall, it was observed that waves III & IV did not grow substantially despite the use of relatively fast scan rates, indicating that the reduced species are scarcely converted back into the starting materials. Therefore, it is reasonable to assume that the reduced forms of cinnamaldehyde are highly reactive/unstable and do not survive

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